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# PATENT SPECIFICATION

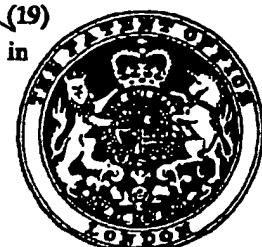
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(21) Application No. 13023/76 (22) Filed 31 Mar 1976  
(31) Convention Application No. 7510253 (32) Filed 2 Apr 1975 in  
(33) France (FR)  
(44) Complete Specification Published 23 May 1979  
(51) INT. CL.<sup>2</sup> C10G 23/02  
(52) Index at Acceptance  
CSE RH

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## (54) PROCESS FOR THE PREPARATION OF A LUBRICATING OIL

(71) We, SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ B.V. a company organised under the laws of The Netherlands, of 30 Carel van Bylandtstraat, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The invention relates to a process for the preparation of a lubricating oil with a low pour point.

It is known to prepare lubricating oils by a two-step hydrotreating of deasphalted waxy mineral oil fractions, followed by a dewaxing step. The yield of lubricating oil with a preset viscosity index often leaves something to be desired.

It has now surprisingly been found that the yield of lubricating oil which can be achieved depends on a proper choice of temperature and catalyst in the two steps, and on the use of the liquid effluent from the first hydrotreating step operationally after removal of gaseous components thereof, as feed for the second hydrotreating step.

Accordingly, the invention provides a process for the preparation of a lubricating oil with a low pour point, which comprises contacting in a first zone a substantially asphaltene-free waxy mineral oil fraction with a supported catalyst containing one or more metals (and/or compounds thereof) of Group VI and/or of Group VIII of the Periodic Table of Elements, in the presence of hydrogen at a temperature of from 390-450°C, contacting in a second zone the total liquid effluent of the first zone, optionally after removal of gaseous components thereof, with an acidic supported catalyst containing one or more metals (and/or compounds thereof) of Group VI and one or more non-noble metals (and/or compounds thereof) of Group VIII of the Periodic Table

of Elements, in the presence of hydrogen at a temperature between 350 and 390°C, and optionally dewaxing all or part of the effluent of the said second zone.

The term substantially asphaltene-free waxy mineral oil fractions stands for mineral oil distilled fractions and deasphalted mineral oil residual fractions.

Suitable starting materials for the process according to the invention are high-boiling hydrocarbon mixtures, e.g. heavy petroleum fractions. Petroleum fractions boiling at least in part above the boiling range of lubricating oil may be used to advantage. As feed for the present process use is, preferably, made of a distillate fraction recovered by vacuum distillation from a residual oil fraction obtained by atmospheric distillation. The boiling range of such a vacuum distillate is usually between 350°C and 550°C. However, deasphalted residual petroleum fractions may also be used.

The process according to the invention is carried out at elevated temperature and pressure and in the presence of hydrogen or a hydrogen-containing gas in the first and second zones. Pure hydrogen may be used, but this is not necessary. A gas with a hydrogen content of 70% or more by volume is perfectly suitable. In practice it will be preferable to use a hydrogen-containing gas originating from a catalytic reforming plant. Such a gas not only has a high hydrogen content but also contains low-boiling hydrocarbons, for example, methane, and a small quantity of propane.

Pressures lower than 50 kg/cm<sup>2</sup> in the first and the second zone are less desirable since they reduce the life of the catalysts while involving the risk of too high an aromatics content in the product, as a result of which the viscosity index is adversely affected. A pressure above 250 kg/cm<sup>2</sup> would require a very costly installation. It is preferable to use a pressure between 100 and 200 kg/cm<sup>2</sup>.

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5 The liquid hourly space velocity and the hydrogen/oil ratio may be selected between wide limits. It is preferred, however, to select a liquid hourly space velocity between 0.1 and 10 kg of oil per hour per litre of catalyst. A liquid hourly space velocity of less than 0.1 kg/hour per litre of catalyst would require uneconomically large reactors for a given degree of conversion, whereas a 10 liquid hourly space velocity of more than 10 kg per hour per litre of catalyst would give only a low degree of conversion into the desired product. The hydrogen/oil ratio is, 15 preferably, between 100 and 5,000 standard litres (litres at 1 bar and at 0°C) per kg of oil. A very low H<sub>2</sub>/oil ratio would adversely affect the life of the catalyst, whereas a very high H<sub>2</sub>/oil ratio would cause a considerable loss of pressure over the catalyst beds, so 20 that much energy for compression would be required for circulating the hydrogen-rich gas.

25 The support of the catalyst of the first zone may be any refractory material. Suitable materials are, for example, alumina (aluminium oxide), silica (silicium oxide), magnesia (magnesium oxide), titanium oxide, zirconia (zirconium oxide), thoria (thorium oxide), boria (borium oxide) and mixtures and compounds of these metal oxides. It is preferred that the supports of the catalysts in the first and second zone consist for more than 50% by weight of 30 alumina. Mixtures of alumina and silica, and in particular alumina and boria are very suitable.

35 In the first zone supported catalysts which contain one or more of the metals nickel, cobalt, molybdenum and tungsten are very suitable, in particular catalysts which contain one of the metals nickel and cobalt and one of the metals molybdenum and tungsten. A catalyst which consists of nickel and tungsten (or compounds, in particular oxides thereof) on an alumina/boria support is mostly preferred in the first zone.

40 The presence of phosphorus and/or fluorine in the catalyst in the first zone is often of advantage. 45 The amounts of the metals present in the catalyst in the first zone may vary between wide limits. Very suitably the catalyst contains from 10 to 30 parts by weight of a Group VI metal and from 2 to 15 parts by weight of a Group VIII metal per 100 parts of catalyst.

50 The metals in the fresh catalysts are very suitable in the oxide form.

55 The effluent of the first zone may be treated in order to remove therefrom undesired gaseous compounds, such as hydrogen sulphide (e.g. by adsorption of H<sub>2</sub>S in an aqueous amine solution, such as a solution of di-isopropanolamine). However, it is preferred to forward the total product emerging

from the first zone into the second zone.

5 The preferred pressure, liquid hourly space velocity and hydrogen/oil ratio in the second zone are equal to those described for the first zone. The temperature of the second zone should be between 350 and 390°C; it should always be lower than the temperature of the first zone.

70 The catalyst of the second zone should be an acidic supported catalyst. By these catalysts are meant those which, when adsorbing the indicator butter yellow (= dimethyl yellow = C<sub>6</sub>H<sub>5</sub>-N=N-C<sub>6</sub>H<sub>5</sub>-N-(CH<sub>3</sub>)<sub>2</sub>) and other still weaker basic indicators, show a colour change of these indicators, indicative of an acid medium.

75 Suitable supports for the acidic supported catalysts are, for instance, compounds of silica and alumina, such as silica-alumina cracking catalysts, compounds of silica and zirconium dioxide, compounds of boron trioxide and silica, compounds of alumina and halogen, such as alumina and fluorine or alumina, silica and fluorine, and the like.

80 The metals (or their compounds) and combinations thereof and the amounts thereof which are very suitable or preferred in the catalyst of the second zone are the same as those of the first zone. Very attractive catalysts for the second zone are nickel and tungsten (or compounds (e.g. oxides) thereof) on an alumina/boria support, and fluorinated nickel and tungsten (or compounds (e.g. oxides) thereof) on a silica-alumina carrier.

85 In many cases it will be attractive to use the same catalyst in the first and the second zone.

90 In case the pour point of the liquid effluent from the second zone is too high, this effluent may be dewaxed as such. However, it is preferred to remove therefrom lower boiling materials (e.g. by distillation) before dewaxing. Very suitably all compounds which have a boiling point up to 400-450°C are removed before dewaxing.

95 The dewaxing may be carried out in any desired manner, e.g. by mixing the liquid to be dewaxed with a suitable liquid (e.g. a mixture of methylethyl ketone and toluene), cooling the mixture to a temperature of about -20°C and removing the solid wax.

100 It is preferred to carry out the dewaxing operation catalytically by contacting the liquid to be dewaxed with a catalyst in the presence of hydrogen. Very suitable catalysts comprise one or more metals or compounds thereof of Group VI and VIII of the Periodic Table supported on a crystalline mordenite. As examples of very suitable metals may be mentioned platinum, palladium and in particular a non-noble metal of Group VI or VIII of the Periodic Table of Elements, preferably tungsten. Pressures of from 40-120 kg/cm<sup>2</sup>, temperatures of from

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300-400°C (in particular of from 300-350°C) and liquid hourly space velocities of from 0.1-2 kg oil per litre catalyst per hour are very suitable.

5. If desired, the effluent of the catalytic dewaxing may be topped in order to remove low-boiling constituents and/or extracted with a suitable extracting agent (e.g. sulphur dioxide, sulfolane) in order to remove aromatic constituents.

**EXAMPLE**

A waxy distillate having a boiling range of between 430°C and 550°C, obtained from a Middle East crude, was passed together with hydrogen over two consecutive catalyst beds at a pressure of 140 kg/cm<sup>2</sup>, a liquid hourly space velocity of 0.8 kg/l of catalyst/hour, the hydrogen/oil ratio being 1750 Nl/kg.

10. The first reactor contained a catalyst having the following composition:

Al<sub>2</sub>O<sub>3</sub> - 57.5%; B<sub>2</sub>O<sub>3</sub> - 6%; WO<sub>3</sub> - 30%; NiO - 6.5%.

15. The composition of the catalyst in the second reactor was:

Al<sub>2</sub>O<sub>3</sub> - 57.5%; B<sub>2</sub>O<sub>3</sub> - 5%; WO<sub>3</sub> - 30%; NiO - 6.5%.

20. In this particular case the composition of the catalyst in the second reactor is therefore identical to that in the first reactor. The temperatures of the two reactors vary, and Table I shows the yield of oil with a viscosity index of 95 (% by weight in relation to the total liquid effluent from the second reactor), obtained after topping at 430°C and after catalytic dewaxing of the said liquid

25. effluent. The catalytic dewaxing was carried out by passing the said liquid effluent (after topping at 430°C) at a pressure of 60 kg/cm<sup>2</sup>, a liquid hourly space velocity of 0.5 kg/l of catalyst/hour, at a temperature of 315°C, over a catalyst consisting of 10% by weight of tungsten (in oxide form) supported on a synthetic mordenite.

30. Similar experiments were carried out, the only difference being the temperatures.

TABLE I

	Temperature of 1st zone	402	401	397	395
	Temperature of 2nd zone	320	340	360	370
50. Yield of oil, %w		50	51	52	58.5

55. Table I shows that the highest yields of oil with a viscosity index of 95 are obtained at a temperature of about 395°C in the first reactor, while the temperature in the second reactor lies between 360°C and 390°C; the yield diminishes as the temperature in the second reactor decreases.

**WHAT WE CLAIM IS:-**

60. 1. A process for the preparation of a lubricating oil with a low pour point, which comprises contacting in a first zone a substantially asphaltene-free waxy mineral oil fraction with a supported catalyst containing one or more metals (and/or compounds

thereof) of Group VI and/or Group VIII of the Periodic Table of Elements, in the presence of hydrogen at a temperature of from 390-450°C, contacting in a second zone the total liquid effluent of the first zone, optionally after removal of gaseous components thereof, with an acidic supported catalyst (as hereinbefore defined) containing one or more metals (and/or compounds thereof) of Group VI and one or more non-noble metals (and/or compounds thereof) of Group VIII of the Periodic Table of Elements, in the presence of hydrogen at a temperature between 350 and 390°C, and optionally dewaxing all or part of the effluent of the said second zone.

70. 2. A process according to claim 1, in which the supports in the first and second zone consist for more than 50% by weight of alumina.

75. 3. A process according to claim 1 or 2, in which the supports in the first and second zone comprise boria.

80. 4. A process according to any one of the preceding claims, in which the catalysts in the first and second zone comprise compounds of nickel and tungsten.

85. 5. A process according to any one of the preceding claims, in which the catalysts in the first zone and the second zone are identical.

90. 6. A process according to any one of the preceding claims, in which the pressure in the first and second zone is between 100 and 200 kg/cm<sup>2</sup>.

95. 7. A process according to any one of the preceding claims, in which the total liquid effluent of the first zone is contacted with the catalyst in the second zone.

100. 8. A process according to any one of the preceding claims, in which the dewaxing is carried out catalytically in the presence of hydrogen with a catalyst which comprises one or more metals or compounds thereof of Group VI and VIII of the Periodic Table of supported on a mordenite.

105. 9. A process according to claim 8, in which one or more non-noble metals of Group VI and VIII of the Periodic Table of Elements are supported on mordenite.

110. 10. A process according to claim 9, in which tungsten is supported on the mordenite.

115. 11. A process according to any one of claims 8-10, in which the catalytic dewaxing is carried out at a pressure of from 40-120 kg/cm<sup>2</sup>, a temperature of from 300-400°C and a liquid hourly space velocity of from 0.1-2 g oil per litre catalyst per hour.

120. 12. A process according to claim 1, substantially as described, with special reference to the Example.

125. 13. A lubricating oil prepared by the process claimed in any one of the preceding claims.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1979.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.